Effect of surface application of ammonium thiosulfate on field-scale emissions of 1,3-dichloropropene

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HIGHLIGHTS

- Five methods and two independent data sets were used to calculate emissions
- Total 1,3-dichloropropene mass loss was $18.4 \pm 6.7\%$ and ranged 12–26%
- Spraying ammonium thiosulfate fertilizer on soil reduced 1,3-D emissions
- Results compared to four related large-scale field experiments

GRAPHICAL ABSTRACT
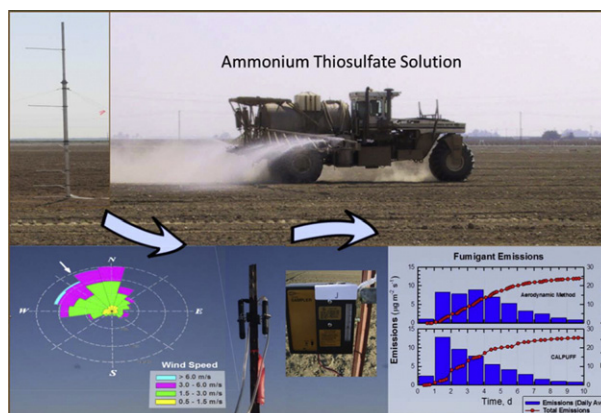
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ABSTRACT

Soil fumigation is important for food production but has the potential to discharge toxic chemicals into the environment, which may adversely affect human and ecosystem health. A field experiment was conducted to evaluate the effect of applying ammonium thiosulfate fertilizer to the soil surface prior to fumigating with 1,3-dichloropropene (1,3-D). The ammonium thiosulfate solution was applied as a spray with minimal water to minimize the effect on emissions from saturating (e.g. sealing) the soil pores with water. Two independent data sets were collected for determining the emission rate. One data set was used with three micrometeorological approaches: aerodynamic, integrated horizontal flux and theoretical profile shape; the other dataset with two indirect, back calculation methods that used the CALPUFF and ISCST3 dispersion models. Using the five methodologies, the 1,3-D emission rate was obtained for 16 days. The maximum emission rates ranged from 7 to 20 μg m^{-2} s^{-1}, the maximum 24-hour averaged emission rates ranged from 5 to 13 μg m^{-2} s^{-1}, and the total 1,3-D emissions ranged from 12 to 26%. Comparing to fumigation without ammonium thiosulfate spray revealed that emissions were reduced from 3% (CALPUFF) to 29% (ADM). Using a simulation model, ammonium thiosulfate spray would be expected to reduce emissions by almost 21%. These data provide evidence that emissions of 1,3-D can be reduced by spraying ammonium thiosulfate fertilizer on the soil surface prior to soil fumigation, and provides another emission-reduction strategy to those recently reported (e.g., deep injection, water seals and organic amendments).

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1. Introduction

Agricultural use of volatile pesticides, and especially soil fumigants, poses a significant risk to human and environmental health, if these compounds are transported away from the target zones or persist in soil. For example, the fumigant methyl bromide (MeBr) was scheduled for phase-out in the year 2005, due to its potential for depleting stratospheric ozone (UNEP, 1992, 1995; Federal Register, 2000). In California, air emission inventories have shown that pesticides, including fumigants, are significant sources of air pollution. From 1976 to 1995, in Fresno County, about 19 tons of pesticides were emitted into the atmosphere each day (ARB, 1978, 1997a, 1997b). This represents 4% of the total organic gas fraction and 16% of the reactive organic gas fraction in this region. Unexpectedly high air concentrations were measured for an agricultural fumigant, 1,3-dichloropropene (1,3-D), which prompted a suspension in California between 1990 and 1994 (CDFA, 1990), until additional research into application controls and mitigations were implemented. With increased restrictions being place on soil fumigation, other pest-control chemicals are needed, such as herbicides. Herbicides may also have significant volatilization potential. For example metolachlor, which has a relatively low vapor pressure compared to soil fumigants (Table 1), has been shown to have significant emission losses when applied to a bare field. Over a 5-year period, total emission losses ranged from 5 to 25% (Prueger et al., 2005) and for an 8-year period, total emission losses were from 6 to 62% (Gish et al., 2011). Total emissions of triallate, a pre-emergent herbicide, applied to bare soil were found to be 30% of the applied herbicide after 7 d (Yates, 2006).

With the phase-out of MeBr, the primary replacement chemicals are generally considered to include: 1,3-D, chloropicrin, and methyl-iso-thiocyanate (MITC) generators (e.g., metam-sodium and basimid) (UNEP, 1995). Soil fumigants have high vapor pressures which ensure relatively high mobility in soil compared to many other herbicides, insecticides and fungicides (Table 1). Fumigants also pose risks to water supplies due to their generally low soil adsorption properties. For example, movement of 1,3-D to groundwater and fate in aquatic ecosystems have been addressed in several studies (Merriman et al., 1991; Obreza and Onterman, 1991; Yon et al., 1991; Schneider et al., 1995; Terry et al., 2008).

Extensive field-scale research on the environmental fate and transport of soil fumigants has been conducted over the last two decades. MeBr emissions for shallow application (i.e., 25 cm) were measured using flux chambers and micro-metrological methods in large scale field experiments for both tarped and untarped conditions. Total MeBr emissions ranged from 32% (Majewski et al., 1995), 49% (Williams et al., 1999) and 62% (Yates et al., 1996) for tarped fields, to as much as 89% for an untarped field (Majewski et al., 1995). This research found that ambient temperature conditions strongly affected emissions for tarped fields, and led to extensive research into understanding and measuring permeability of tarp materials (Papiernik et al., 2011). Applying MeBr deeper in soil (i.e., 60 cm) was found to significantly reduce MeBr emissions (21% of applied; Yates et al., 1997) compared to a shallow-tarped fumigation (64% applied; Yates et al., 1996). As MeBr use has phased out, research has been redirected to the study of emissions from 1,3-D. Large-scale field experiments have been conducted to determine if using irrigation water to create a surface water seal (Yates et al., 2008), applying composted municipal green waste to create a reactive surface barrier (Yates et al., 2011), or injecting 1,3-D deeper in soil (Yates et al., 2016) reduces 1,3-D emissions compared to standard injection methodology (Yates et al., 2015).

Previous research has shown that creating a surface water seal reduces fumigant emissions (Jin and Jury, 1995). The principal behind this approach is that liquid-phase diffusion of a pesticide is orders of magnitude less than diffusion in the gas phase. Therefore, if saturation of the soil pores at the soil surface can be maintained, fumigant diffusion into the atmosphere will be reduced. This approach has been subsequently demonstrated in laboratory (Gan et al., 1998) and field experiments (Sullivan et al., 2004; Yates et al., 2008; Gao and Trout, 2007).

Applying ammonium thiosulfate (ATS), or other thiosulfate solutions (i.e., potassium thiosulfate, sodium thiosulfate, etc.) to the soil surface has been proposed as a method to create a reactive soil layer (Zheng et al., 2005) that can rapidly degrade 1,3-D at the surface before entering the atmosphere, which reduces the amount of 1,3-D available for emissions. Significant reductions of 1,3-D emissions have been observed in laboratory experiments when ATS was applied to the soil surface in water (Gan et al., 2000a). This experiment also found that increasing the amount of water and/or amount of ATS decreased the emission rate. Other researchers have confirmed this result by showing that thiosulfate reduced 1,3-D emissions when applied with irrigation water in field plot (Gao et al., 2008) and in laboratory experiments (Qin et al., 2007; McDonald et al., 2008) settings. However, no research could be found differentiating the effects of the surface water seal and the effects of the ATS.

When attempting to create a reactive surface layer, a complication for field-scale fumigation by shank injection is that adding an ATS solution to the soil surface may not always be practical. This could be due to lack of an available irrigation system, increased costs for the irrigation water, or regions that experience limited water availability for anything except crop production. Furthermore, adding sufficient quantities of ATS needed to react with 1,3-D and reduce emissions, could be above typical fertilization rates and could increase costs and complicate fertilizer management. These factors make the use of a reactive surface barrier (i.e., ATS-water) problematic unless ATS and water applications can be minimized. To this end, we describe an experiment to test the use of ATS to create a reactive surface barrier. The target ATS application rate needed to be feasible in terms of fertilizer quantities and water application. Since an irrigation system was not available at the field site, the land-owner proposed applying the ATS-water mixture using a tank-mounted truck appropriate for field spraying (i.e., a "floater"). The aim was to minimize the quantity of water applied to the soil surface to test the effectiveness of ATS without the confounding effects of surface water sealing. If successful, this approach would be a simple, and low cost, method to reduce 1,3-D emissions in large fields.

2. Methods

The experiment to measure 1,3-D emissions was conducted in a large agricultural field located approximately 5 miles north of Buttonwillow, CA. The field soil is classified as Milham sandy loam (fine-loamy, mixed, thermic Typic Haplargids) and was found to have 1% organic matter content in the upper soil surface (e.g., 10 cm). The field was managed according to standard fumigation practices and was irrigated so that the soil condition was suitable for fumigation with a water content approximately 0.2 (cm^3 cm^{-3}). The fumigant 1,3-dichloropropene (1,3-D, CAS: 542-75-6) was applied by a commercial applicator using a standard fumigation practices. The injection tractor had a 450 cm wide tool bar attached that held 9 evenly-spaced shanks. The fumigant application depth was 46 cm (i.e., 18 in.), the 1,3-D applied was 470 kg ± 1 kg (i.e., application rate of 164 kg/ha), and the field shape was approximately square and 2.87 ha in area. The experimental schematic is shown in Fig. 1.

Table 1
Pesticide properties. K_d: soil distribution coefficient assuming 1% soil organic carbon content; K_H: Henry's Law coefficient.

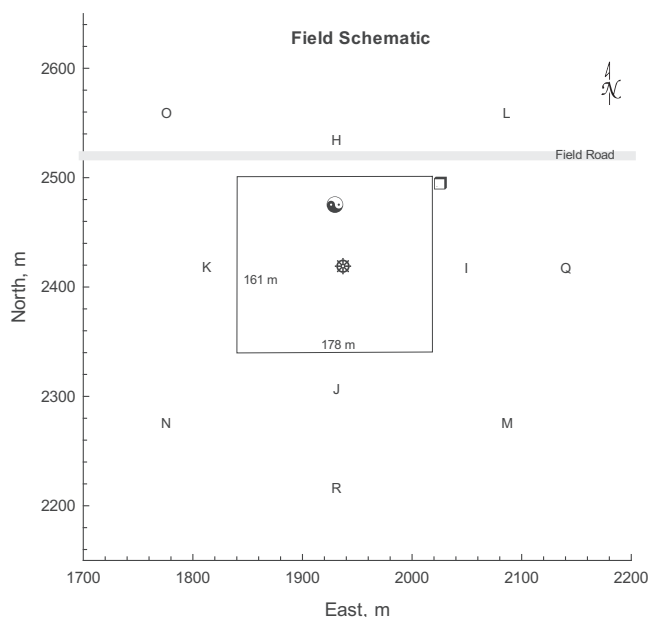| Pesticide	MolWt	Boil Pt. °C	Solubility mg L^{-1}	Vapor pres. mm Hg	K_H [−]	K_d mL g^{-1}
MeBr	95	3.6	13,400	1420	0.29	0.22
chloropicrin	164	112	2270	18	0.07	0.62
1,3-D	111	104	2250	29	0.08	0.32
MITC	73	119	7600	20	0.01	0.24
triallate	305	117	4	1.1×10^{-4}	4.5×10^{-4}	24.0
metolachlor	284	100	530	3.1×10^{-5}	9×10^{-7}	2.0

Fig. 1. Field layout and positions of sampling equipment.

A tanker truck with a spray boom was used to apply ammonium thiosulfate (ATS) solution to the soil surface. The target application rate was 471 kg/ha (i.e., 420 lbs./ac) thiosulfate at a 1.7:1 (thiosulfate:fumigant) molar ratio. This application rate was a compromise between the desire to have a high molar ratio (e.g., 4:1) to create a strongly reactive soil layer and fertilizer recommendations. To measure the amount of ATS actually applied to the field, three transects containing a total of 40 sampling plates were placed on the soil surface to collect samples. The average of the samples revealed that the actual application rate was 538 ± 97 kg/ha. The measured molar ratio was 1.8:1; which is close to the target value.

For Milham sandy loam, soil degradation of 1,3-D has been reported to have a half-life of approximately 5 days (Ashworth and Yates, 2007). A literature estimate for the organic carbon distribution coefficient is $K_{oc} = 32$ mL g^{-1} (Wauchope et al., 1992) and the Henry's Law constant has been reported to be $K_h = 0.04$–0.06 (Leistra, 1970).

2.1. Air measurements of 1,3-D

The 1,3-D air concentration was measured at 10, 40, 80, 150, 250 and 400 cm above the ground surface using a vacuum system to move air through XAD-4 sampling tubes (SKC 226–175, SKC, Incorporated, Fullerton, CA§) at a nominal flow rate of 150 cm^3 min^{-1}. At the beginning of the experiment, the sampling schedule consisted of 3–h sampling periods during the daytime and a 12–h sampling period at night. On days 4 and 10, respectively, the daytime sampling intervals were increased to 6 and 12 h so that sufficient mass was collected for residue analysis. The field sampling protocol was: (a) disconnect the XAD-4 tubes from the sampling mast after each time interval, (b) place caps on the ends of the tubes, (c) store samples on ice and transport samples to a nearby freezer for temporary storage, and (d) periodically transport samples to the laboratory in an ice chest and place into a −70 °C freezer until analysis. After a new XAD-4 tube was installed, an in-line flow valve was adjusted to maintain the 150 cm^3 min^{-1} flow rate. The flow meters were continuously monitored so that the total volume of air passing through the XAD-4 was obtained for each sampling period.

The 1,3-D concentrations in the soil gas phase were collected at 2 locations in the field (Fig. 1). The sampling protocol involved the use of hollow guide rods which contained a stainless-steel tube (inner

diameter 0.01″) with an open port installed at 5, 10, 25, 50, 75 and 100 cm depths. During sampling, a gas-tight syringe was connected to the stainless steel tube and 50 mL of the soil pore space was drawn through an XAD-4 tube. All sampling equipment consisted of non-adsorbing, low permeability materials (e.g., stainless steel, glass, Teflon, etc.).

2.2. Meteorological measurements

Measurements of wind speed at 15, 35, 75, 155, 235 and 355 cm above the ground surface were obtained with Thornthwaite anemometers (CWT-1806, C.W. Thornthwaite Assoc.). Wind speed and wind direction measurements were also obtained at 20, 160 cm above the ground surface with Windsonic 2-D, (Gill Instruments, Ltd) anemometers and at a height of 10 m with a 5305 Wind Monitor (R.M. Young, Traverse City, MI). Air temperature gradient measurements were obtained by placing fine wire thermocouples (FW3, Campbell Scientific, Inc.) at 20, 40, 80 and 150 cm above the soil surface. Other measurements collected included incoming solar radiation (LI-200S, LI-COR, Inc.), net solar radiation (Q-6, Radiation and Energy Balance Systems, Inc), relative humidity and temperature (HMP35C, Campbell Scientific, Inc.), and barometric pressure (Vaisala PTA-427, Campbell Scientific, Inc.).

2.3. Methods for measuring the volatilization rate

Three micrometeorological methods and two regulatory methods were used to obtain the volatilization rate: aerodynamic (Parmele et al., 1972), integrated horizontal flux (Denmead et al., 1977), theoretical profiles shape (Wilson et al., 1982) methods; and back-calculation methods using CALPUFF (Scire et al., 2000), and the ISCST3 (Ross et al., 1996; Barry et al., 1997; Cryer et al., 2015). For the aerodynamic method (ADM), gradients of wind speed, temperature and fumigant concentration are collected over a relatively large and spatially–uniform source area (Parmele et al., 1972). The equation used to obtain emissions, f_z, with the ADM was (Rosenberg et al., 1983)

$$f_z = -k^2 \frac{\left[\overline{C}_2(t) - \overline{C}_1(t)\right] \left[\overline{u}_2(t) - \overline{u}_1(t)\right]}{\phi_m(t) \; \phi_c(t) \quad \ln(z_2/z_1)^2} \tag{1}$$

where k is von Karman's constant ($k = 0.4$), $\overline{C}$ and $\overline{u}(t)$ are period-averaged concentrations and wind speeds, z is distance above the surface, and ϕ_m and ϕ_c are stability corrections for momentum and 1,3-D. The quantity $1/(\phi_m \; \phi_c)$, an atmospheric stability correction factor, was used as an indicator of effect of atmospheric stability on emissions.

The wind speed and concentration gradients were computed by linear regression (i.e., scalar vs natural logarithm of height) to calculate an emission rate using the measurements between the surface and 150 cm height. Therefore, the gradient measurements were representative of a height that was 1–2% of the upwind fetch distance.

The integrated horizontal flux (IHF) method requires fumigant concentration and horizontal wind speed measurements at several heights above the soil surface (Denmead et al., 1977). This method uses a mass balance approach to estimate the volatilization rate and has an advantage that corrections for atmospheric stability are not required.

The theoretical profile shape (TPS) method combines the trajectory simulation model of Wilson et al. (1982) and the measurement of wind speed and fumigant concentration at a single height to estimate the volatilization rate. This method does not require large upwind fetch distance and is relatively insensitive to atmospheric stability, so stability corrections are unnecessary. Further information on the use of these approaches to measure fumigant emissions can be found in the literature (Majewski et al., 1995; Yates et al., 1996; Yates et al., 1997, 2008, 2011, 2015).

The total fumigant mass lost after application to soil as a function of time can be found using

$$f_{total}(t) = \iint\limits_{x,y} \int\limits_{0}^{t} f_z \, d\tau \, dy \, dx = A \int\limits_{0}^{t} f_z \, d\tau \qquad (2)$$

where f_z is the volatilization rate ($\mu g \, m^{-2} \, s^{-1}$), τ represents time, and (x, y) are horizontal coordinates in the treated region of the field. For a spatially uniform source, the right-hand equation can be used where A is the area (m^2) of the treated field.

2.4. Chemical analysis

XAD-4 sampling tubes were used to collect 1,3-D concentrations in the atmosphere at the field site. These tubes have two sorbent beds, the front bed containing 400 mg of XAD-4 and the back bed containing 200 mg.

For analysis, the sampling tubes were removed from the freezer, warmed to room temperature, the tube was cut and each sorbent bed was transferred to individual head-space vials (21 mL). Next, n-hexane (4 mL) was added to each vial, which was immediately sealed with an aluminum cap with Teflon-lined septum. After shaking the vials for 30 min in a reciprocating shaker, 1 mL of the supernatant was transferred to a GC-vial (2 mL), which was capped and then stored in a −70 °C freezer until analysis by gas chromatography.

Analysis of 1,3-D concentration was obtained with an Agilent 6890 series gas chromatograph (Agilent Technologies, Palo Alto, CA) with a micro-electron capture detector (μECD) and DB-VRX column (30 m × 0.25 mm). Analysis conditions: inlet, oven and detector temperatures, respectively, were 240, 90 and 290 °C; nitrogen flow rate was 60 mL min^{-1} and the injection volume was 4 μL.

The limit of quantification (LOQ) and the limit of detection (LOD) were found to be, 0.14 μg/tube and 0.05 μg/tube, respectively. Preliminary tests conducted with an air flow rate of 150 cm^3 min^{-1} revealed that the XAD-4 extraction efficiency was 86 ± 5% and that recovery of the 1,3-D mass from both sorbent beds was 98%.

2.5. Field layout

The field layout and sampling locations are shown in Fig. 1. Two independent data sets were collected for determining the emission rate. The on-field measurements were located near the center of the field and included 1,3-D concentrations, wind speed and direction, and air temperatures at multiple heights (i.e., ✲). The off-field measurements included 1,3-D concentrations (letters H–Q), wind speed and wind direction at 150 cm height. In addition, 1,3-D concentration in the soil were obtained (i.e., ◔) and soil temperature and heat flux (i.e., ▢). The off-site samples H–K, L–O, and Q–R, respectively, were positioned to be 30, 90 and 120 m from the nearest field boundary.

3. Results and discussion

3.1. Fumigant concentrations in air

Concentrations of 1,3-D were collected at several heights in the center of the field and at locations that were positioned to be 30, 90 or 120 m from the field boundary. The 24-h averaged concentrations at a height of 150 cm above the surface are shown in Fig. 2.

The 24-h average concentrations obtained from the middle of the field (Fig. 1, site ✲) were considerably higher than those measured at sampling locations positioned at 30 to 120 m surrounding the field (see Fig. 1, sites H-Q). For example, the largest value at the field center was 72 μg m^{-3}, and occurred on day 2. The highest value at 30 m from the field boundary was 33 μg m^{-3} and occurred on day 1. For distances 90 and 120 m, the 24-h average concentrations were very similar
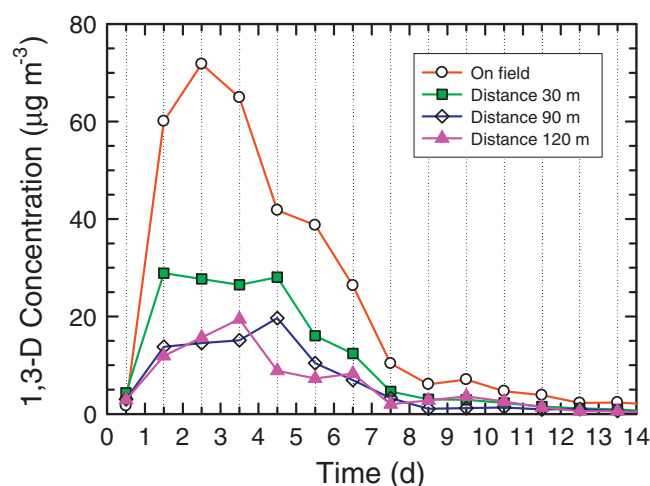

Fig. 2. Concentration (μg m^{-3}) of 1,3-D in the atmosphere during the experiment. The values shown are daily (24 h) averages and were collected at 150 cm height.

and generally <20 μg m^{-3}. The 24-h average concentrations in the middle of the field are unaffected by wind direction and accumulate mass for the entire sampling period. This leads larger 24-h values compared to the 30–120 m locations where the resultant concentrations are strongly affected by wind direction and may not accumulate mass for the entire sampling period (i.e., when sampler is upwind from field). Another factor affecting the 24-h averages relates to the position of the samplers. For example at the 90 m sample locations (e.g., sampler 'M'), the apparent distance (a measure of the distance from the sampler to the field edge by moving directly upwind) to the field boundary is 90 m only for a NW to SE wind direction. For all other southeasterly wind directions, the apparent distance would be >90 m. This, and the natural variations in wind direction during the sampling period, provides an explanation for the similar concentration for 90 and 120 m distances shown in Fig. 2. The overall trend was the same for all distances, where the concentration levels were initially low, then increased to a maximum at approximately 2 days after fumigation, and then became very low by the 16 day.

Next, consider all of the individual measurements collected over the course of the experiment, both measurements located onsite and at positions H–Q surrounding the field. The maximum concentrations for short time-periods (i.e., 2–3 h) at the center of the field (✲) were similar to the maximum concentrations located around the field (H-Q). For example, at 1.7 days, the on-field concentration was 71 μg m^{-3}, and maximum short-term concentrations at 30, 90, and 120 m were, 111 (site J), 34 (site M), and 59 (site R) μg m^{-3}, respectively. However, if the short-term concentrations for the equidistant samplers surrounding the field are averaged (i.e., H–K for 30 m, etc.), the results are similar to the 24-h values shown in Fig. 2. This indicates that offsite concentrations are strongly dependent on meteorological conditions, especially wind direction, and that averaging can significantly reduce reported concentration values. For some data uses (e.g., risk assessment), this is unlikely appropriate and the maximum concentration for all the individual samples should be used.

The large concentrations at the beginning of the experiment are due to larger 1,3-D gradients in soil immediately after fumigation and rapid upward diffusion caused by the presence of soil fracture zones caused by the fumigation shanks. Rapid movement along the shank at early times has been shown to produce more uniform and higher soil concentrations above the injection depth compared to injection methods that do not produce a shank fracture (Yates, 2009). At later times, the fumigant volatilizes and degrades in soil so atmospheric concentrations lessen.

3.2. Volatilization of 1,3-D

Fig. 3 shows time series for the emission rate (i.e., flux density) calculated using the ADM, IHF, and the TPS methodologies. These time series have a similar overall behavior with increasing emission rates early in the experiment, peaking after 3–4 days, followed by reducing emission rates that become very low after about 10 days after application (i.e., shaded bars). Super imposed are daily cycles where high emission rates occur generally after midnight with low values occurring late afternoon and early evening. While this general tendency is expressed, at any particular time point, there can be fairly large differences in volatilization rates. Occasionally, the temporal trends for these methods are in opposition, for example, 12–18 h after injection (i.e., 1–1¼ days), the ADM emission rate is increasing while the IHF and TPS emission rates are decreasing. Continuing until shortly after 1½ days, the reverse occurs. There are also differences in the magnitude of the calculated emission rates. The maximum measured flux values for the ADM, IHF and TPS methods were 19.4, 6.7, and 7.6 $\mu g\ m^{-2}\ s^{-1}$, respectively. In general, the IHF and TPS emission rates, respectively, were found to be 56% and 54% lower than the ADM method.

Consider the shaded areas in Fig. 3, it is clear that the maximum 24 hour-averaged flux values were lower than the short-term emission rates and produced a smoother curve. The maximum values for the 24-hour averaged emission rate obtained from the ADM, IHF and TPS methods, respectively, were 8.9, 4.7 and 5.2 $\mu g\ m^{-2}\ s^{-1}$.

Given that turbulent mixing, energy inputs and unstable atmospheric conditions are commonly most pronounced during midday (Rosenberg et al., 1983) it would be expected that volatilization rates would also peak midday. However, for this experiment the highest flux rates occurred during the midday only for day 1 and 2; afterwards the highest values occurred shortly after sunrise. Also, all three methods show a decreasing flux rate beginning before noon and continuing until afternoon or evening. A possible explanation is that the soil surface is drying due to the input of solar energy, which increases the 1,3-D vapor phase adsorption to the upper layer of soil. Spencer et al. (1969) showed that vapor phase adsorption strongly binds a volatile herbicide to soil particles as the water content decreases to low levels. This process is highly non-linear and temperature dependent. However, a literature search was unable to reveal if 1,3-D vapors are also strongly adsorbed at very low soil water content. If this process occurs for 1,3-D, then the emission rate would increase when the water content of the soil surface is replenished due to water vapor movement to the surface, redistribution, and/or irrigation/precipitation/dew formation. Under non-irrigated, non-rainfall conditions, the increased emission rate would most likely occur during early morning hours and low

emission rates would occur in the afternoon as solar heating dries the surface soil.

The temporal pattern for the flux density is similar for the CALPUFF and ISCST3 regulatory emission methods (Fig. 4). Under these field and treatment conditions, the peak period averaged flux occurred between 2.0 days (ISCST3) and 3.4 days (CALPUFF); whereas the peak for the ADM method was at 4.3 days (Fig. 3). The maximum flux for the CALPUFF and ISCST3 methods, respectively, were 19.7 and 15.6 $\mu g\ m^{-2}\ s^{-1}$ and the maximum 24 h-averaged flux values, respectively, were 12.8 and 8.8 $\mu g\ m^{-2}\ s^{-1}$.

The time course for the total emissions of 1,3-D during this experiment are shown in Fig. 3 and Fig. 4 (insets). It is clear that the IHF and TPS methods (Fig. 3) provide essentially the same total emission rate; their estimated values were 12.5%. The total emission rate obtained from the ADM and CALPUFF methods, respectively, were 25% and 26.3%, which is about twice as large as the values of the IHF and TPS methods (Table 2). The total emission for the ISCST3 method was in between the ADM/CALPUFF and IHF/TPS methods, with a value of 16%.

Atmospheric turbulence and stability are thought to affect emissions of volatile pesticides from soil. To investigate the relationship, an atmospheric stability correction factor, i.e., $1/(\Phi_m \Phi_c)$ was calculated to provide a means of determining correlations between atmospheric stability and the peak ADM emission rates. Shown in Fig. 5 are the measured emission rates superimposed over the stability correction factor (grey bars). According to Eq. 1, it is clear that the atmospheric stability affects the emission rate. There are periods where they coincide (i.e., days 1 and 2), but at other times the correlation between peak correction factor and peak emission rate is rather weak. For many days, the peak stability correction factor occurs near solar noon, but the peak emission rate occurs several hours earlier. This provides evidence that other factors are affecting the emission rate and controlling the timing of the peak flux.

Table 2 provides summary information for the emission measurements. The ADM and CALPUFF methods produced similar results and had maximum emission rates of 19.4 and 19.7 $\mu g\ m^2\ s^{-1}$, which was followed by the ISCST3 method (15.6 $\mu g\ m^2\ s^{-1}$), and by the IHF and TPS methods (6.7 and 7.6 $\mu g\ m^2\ s^{-1}$). The timing of the maximum emission rate varied between calculation methods but all maxima occurred from 1.8–4.3 days. Ranking the total emissions from high to low has a similar sequence as the maximum flux: ADM ≈ CALPUFF > ISCST3 > IHF ≈ TPS.

The total emission estimates from the ADM, IHF, TPS, ISCST3 and CALPUFF methods, respectively, are 25.0%, 12.5%, 12.5%, 15.9%, and 26.3% of the applied 1,3-D. The average and standard deviation of the total emission from the 5 methods is, respectively, 18.4 ± 6.7% and for the ADM, ISCST3, and CALPUFF methods is, respectively, 22.4 ± 5.7%.
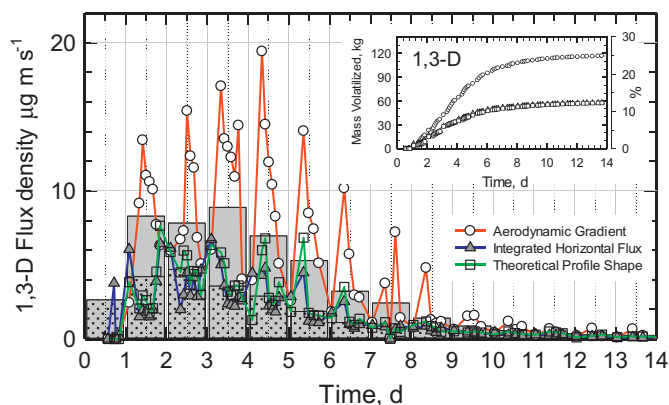

Fig. 3. Emissions of 1,3-D ($\mu g\ m^{-2}\ s^{-1}$) into the atmosphere during the experiment. The circles are for ADM, triangles for IHF, and squares for TPS methods. The shaded values (bars) shown are daily (24 h) averages; solid color is ADM, stippled is IHF. Inset is total emission (kg, and %) for each method.
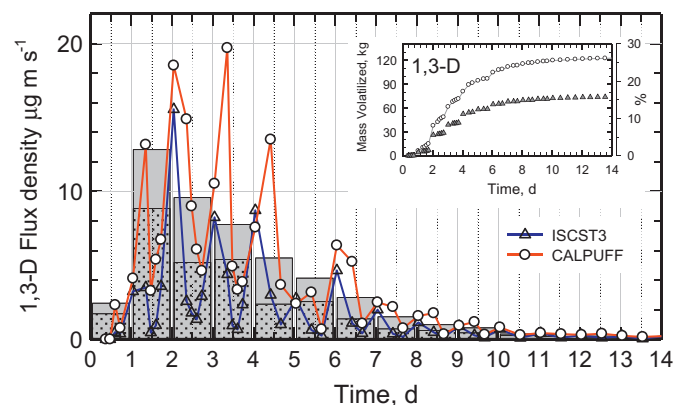
Fig. 4. Emissions of 1,3-D ($\mu g\ m^{-2}\ s^{-1}$) into the atmosphere during the experiment. The circles are CALPUFF emission and the triangles are from ISCST3. The shaded values (bars) shown are daily (24 h) averages; solid color is CALPUFF, stippled is ISCST3. Inset is total emission (kg, and %) for each method.

Table 2
Summary of emission measurements.

	ADM	IHF	TPS	CALPUFF	ISCST3
Maximum emission rate, (μg m^2 s^{-1})	19.4	6.7	7.6	19.7	15.6
Time of maximum emission (days)	4.3	3.1	1.8	3.4	2.0
Maximum 24-h average emission rate, (μg m^2 s^{-1})	8.9	4.7	5.2	12.8	8.8
Total emissions, (kg)	117.4	58.7	58.9	123.5	74.6
Total emissions, (% of 1,3-D applied)	25.0	12.5	12.5	26.3	15.9

While there are clear differences in the emission estimates, the experimental results are consistent with the uncertainty analyses for methods to calculate field-scale emissions (Majewski, 1997; Wilson and Shum, 1992), which have been shown to be accurate to approximately ± 20–50%. Majewski (1997) showed that the accuracy of methyl bromide emissions obtained from the ADM was approximately ± 50%. This result was based on an analysis using regression of the log-linear wind speeds and concentrations with respect to height, and should also apply to 1,3-D which has a log-linear concentration profile. Wilson and Shum (1992) found that for large fields with surface roughness lengths below 10 cm, the experimental accuracy should be within approximately ± 20%. This analysis was based on a Lagrangian stochastic model and also provided guidelines that can be used in the design of field experiments.

3.3. Soil gas phase concentration

Shown in Fig. 6 is the soil gas-phase concentration (A) and the soil water content (B) at various times after field application of 1,3-D (see Fig. 1). The soil water content remained relatively constant throughout the experiment and averaged 0.19 ± 0.05 cm^3 cm^{-3} at the start and 0.16 ± 0.03 cm^3 cm^{-3} at the end of the experiment. During the first
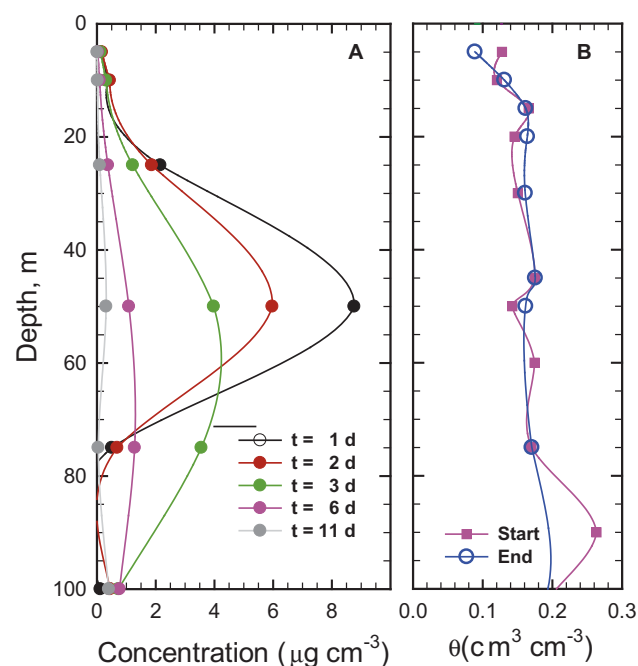
Fig. 6. Soil gas concentration (μg cm^{-3}) of 1,3-D as a function of depth in the soil and time after fumigation (A). In B, the initial and final soil water content (cm^3 cm^{-3}) is presented.

24 h, the 1,3-D soil gas-phase concentration at the injection depth exceeded 8 μg cm^{-3} and steadily declined each day in response to soil diffusion in the liquid and gas phases and soil degradation acting in concert to reduce the concentrations to low levels, i.e., <0.5 μg cm^{-3} by day 11. By day 6, the soil 1,3-D concentrations below 50 cm were nearly constant.

3.4. Comparisons of experiments

Since 2005, five field-scale experiments were conducted at the same field site to serve as an experimental control and to test several emission-reduction strategies, such as using irrigation to create a surface water seal (Yates et al., 2008), applying composted municipal green waste to create a reactive surface barrier (Yates et al., 2011), injecting deeper in soil as a means to reduce 1,3-D emissions (Yates et al., 2016), and applying an ammonium thiosulfate spray to the soil surface to create a reactive surface layer, which is the subject of this paper. A summary of results from the five experiments is shown in Table 3.

The maximum short-term emission rate is highly variable across the experiments. Interestingly, the highest reported value occurred during an experiment utilizing surface water seals to reduce emissions. It seems plausible that sealing the soil surface restricted the diffusion process and caused an increased soil 1,3-D concentration near the surface below the seal. As soon as the soil pores drained, it would appear that 1,3-D escaped and produced the highest observed rate (i.e., 59.8 μ m^2 s^{-1}). However, the surface water seal undoubtedly increased the 1,3-D residence time, during the 16-day experiment, which likely increased degradation and decreased total emissions (i.e., 15.3%), compared to the 2007 experiments.

The maximum 24-hour emission values for the 2005 experiments were lower than the values from the 2007 experiments. This suggests that utilization of surface irrigation or organic soil amendments may provide more effective emission-reduction when compared to deep injection and use of a surface spray of ammonium thiosulfate. The additional material cost of ammonium thiosulfate is also a disadvantage of this approach.

It is interesting that the ISCST3 back-calculation method consistently produces lower total emissions compared to the CALPUFF method.
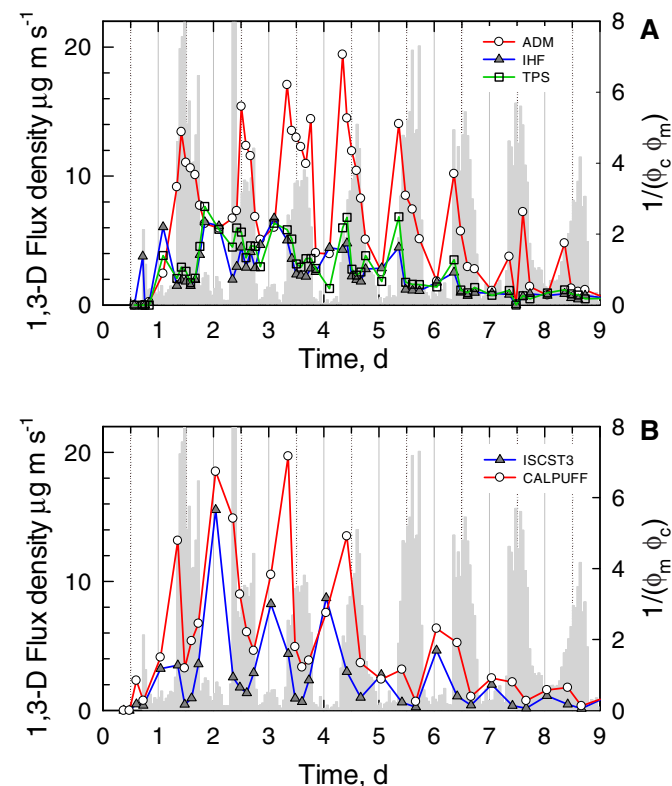
Fig. 5. Superposition of the atmospheric stability correction factor (grey bars) and emissions of 1,3-D (μg m^{-2} s^{-1}) for each method. Fig. 5A show a comparison for the ADM, IHF, and TPS methods. Fig. 5B shows a comparison for the CALPUFF and ISCST2 methods.

Table 3
Summary of the Buttonwillow emission experiments. Information on the maximum short-term 1,3-D emission rate (μg m^2 s^{-1}), the maximum 24-h average emission rate (μg m^2 s^{-1}), and total emissions (% of 1,3-D applied) is provided.

	Surface irrigation (2005)	Composted green waste (2005)	Control (2007)	Deep injection (2007)	ATS surface spray (2007)
			ADM		
Maximum emission rate	59.8	23.2	25.0	32.3	19.4
Maximum 24-h average	8.0	4.4	15.7	10.8	9.8
Total emissions	15.3	8.2	35.4	26.7	25.0
			CALPUFF		
Maximum emission rate	9.5	6.9	29.9	33.4	19.7
Maximum 24-h average	4.9	2.7	12.1	11.6	11.9
Total emissions	10.0	4.0	27.2	26.1	26.3
			ISCST3		
Maximum emission rate	7.1	2.4	11.7	13.2	15.6
Maximum 24-h average	3.3	1.9	6.5	6.7	7.3
Total emissions	6.0	3.9	16.2	15.8	15.9

ISCST3 is a steady-state Gaussian plume model that uses a 1-h time step for characterizing meteorological conditions. During a 1-h period with highly variable winds, the results from ISCST3 would diverge from actual field measurements. CALPUFF is likely more accurate than ISCST3 because it is a non-steady state puff model that tracks chemical movement in a more natural manner, where the puffs can move in any direction in response to short-term wind conditions. Also, the model time step is flexible, so that high frequency wind measurements can be used for the simulation.

An unresolved issue is whether Deep Injection or ATS Surface Spray provides significant emission reduction compared to the Control. Comparing the total emissions for the ADM approach, deep injection or ATS treatment leads to a 25–30% reduction in emissions. However, based on CALPUFF approach, the reduction in emissions is much less (i.e., ~4%). Given this discrepancy, the mathematical volatilization model of Yates (2009) was used to obtain predictions of the emission rate for shank injection at 46 cm (control) and at 61 cm (deep). The model was used in predictive mode so model parameters were either directly measured or obtained from literature values. The model predicted that total emissions for control and deep injection, respectively, would be 27% and 21%, which leads to a reduction in emissions of 22%. To further corroborate the other field measurements, the irrigation, organic matter and ATS treatments were simulated using a numerical model. The predicted emission rates were 12% (surface irrigation) and 3% (composed green waste). These simulations suggest that the results from the field experiments are valid and that the reduction in emissions from the ATS treatment could be as high as 30%.

Gan et al. (2000b) presented data that can be used to obtain the second-order rate coefficient, which enables mathematically simulating the ATS and 1,3-D reaction process in soil. Using this data, a second-order reaction coefficient (1.6×10^{-4} cm^3 μg^{-1} h^{-1}) was computed and used to simulate emissions with, and without, an ATS spray. Predicted total emissions without an ATS spray was 30.5% and with the ATS spray was 24.1%. Therefore, the predicted reduction in total 1,3-D emission after spraying the surface with an ATS solution was 21%.

3.4.1. Soil gas measurements

Two replicated soil gas concentration profiles were obtained for each of the 2007 experiments and both soil-gas profiles produced similar concentration levels for this experiment. The soil concentration measurements on day 1 for this experiment (Fig. 6) were 14 times higher than the measurements from the Control Plot (Yates et al., 2015), but were 60% lower than the Deep Injection Plot (Yates et al., 2016). For the "Control Plot" one of the replicates had very low concentrations possibly due to a problem installing the soil-gas samplers (i.e., plugging). Natural spatial variability could also have caused low values in the Control Plot if a soil structural element impeded fumigant lateral diffusion to the samplers. The higher concentration on day 1 observed in the Deep Injection Plot could have been caused more rapid 1,3-D diffusion

to the samplers since the injection shank produced large soil fractures at this site, which were not observed in the other fields. This may have aided in more rapid lateral diffusion.

4. Conclusions

The results from a series of five field experiments has shown that emissions of 1,3-D can be reduced compared to traditional fumigation methodology. Applying an ATS solution to the soil surface as a low-water-volume spray is practical in terms of common farming practices and equipment, and has the potential to reduce emissions by as much as 20%.

The purpose of creating a reactive surface layer was to increase soil degradation of 1,3-D before diffusion into the atmosphere. It has been recognized that reducing 1,3-D concentration in soil could potentially affect pest control. Applying ATS as a low-water-volume spray reduces the depth of the reactive zone and should have a less impact on pest control compared to applying ATS with larger volumes of water. In both laboratory and field research studies (Gan et al., 2000a, 2000b), it was shown that application of ATS to the soil surface did not reduce the effectiveness of 1,3-D in controlling nematodes or tomato yields.

This study has also revealed that predictive mathematical modeling can provide essentially identical total emission estimates as much more expensive, complex and time consuming field experiments, especially considering the variability found in the experimental emission data. Accurate mathematical models are also valuable to parameterize the flux density input, which is required to utilize air dispersion models for the purposes of developing buffer zones and assessing bystander exposure and risk.

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